

# **XAFS of Transition Metal Molecular Sieves for Artificial Photosynthesis**

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## **PROJECT DESCRIPTION**

Photochemical synthesis of a fuel by direct reduction of  $\text{CO}_2$  using visible light and  $\text{H}_2\text{O}$  as electron source is one of the most attractive, yet unrealized goals in solar energy-to-fuel conversion. Photosynthesis of methanol for large scale use in fuel cells is considered as a promising option for replacement of fossil fuel combustion as a means of power generation. We propose to explore transition metal framework substituted microporous solids containing two different metals as a new type of photoreactor for  $\text{CO}_2$  reduction by  $\text{H}_2\text{O}$ . The most critical and challenging aspect of this task is reliable characterization of such bifunctional molecular sieves and the verification of their structural integrity under use. X-ray absorption techniques, especially EXAFS (Extended X-Ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge Structure), are the best tools for this type of solid. The purpose of the project is to (i) explore the synthesis of bifunctional framework metal sieves, (ii) initiate EXAFS and XANES studies at the ALS in order to establish an efficient approach for the characterization and screening of these new materials.

The project consists of XAFS experiments on two established microporous materials,  $\text{TiAlPO}_4\text{-5}$  and Ti silicalite in order to elucidate the local structure of framework Ti centers. In parallel, the synthesis of novel mono-substituted sieves ( $\text{RuAlPO}_4$ ) and bifunctional materials ( $\text{TiFeAlPO}_4$ ) will be explored and the samples characterized by XAFS measurements. The project involves the design and fabrication of an XAFS sample stage consisting of a cryostat (77-700K), a holder for 12 samples, and detectors for measurement in transmission or fluorescence mode. Experiments will be conducted at BL 9.3.1, whose energy range spans the K-edge of Ti and L-edge of Ru.

## **RESULTS**

A sample holder featuring 12 sample positions and variable temperature option (77-700K) was designed and fabricated. An XYZ manipulator allowed convenient alignment of each sample (pressed wafer of molecular sieve crystallites) in the X-ray beam. The sample holder was mounted on an XAFS endstation built by Dr. Melvin Klein at ALS Beamline 9.3.1, which covers the energy range 2-6 KeV. Detection is either in transmission or in fluorescence by a retrievable Si photodiode, mounted at a right angle.

With this new setup, we have recorded XANES spectra of Ti substituted aluminophosphate (TAPO-5) and silicate (TS-1) sieves synthesized in our laboratory. A sharp  $\text{A}_1\text{-T}_2$  pre-edge absorption at 4968 eV characteristic of Ti centers in tetrahedral

framework sites was detected in transmission and fluorescence modes. Using samples with Ti concentrations varying between 0.5 and 3 percent, the width and intensity of the pre-edge band revealed that materials with Ti content of 1.5 percent or lower exhibit perfect framework substitution (no extraframework Ti present). Characterization of these Ti substituted sieves by XAFS measurements furnished the basis for two mechanistic studies on CO<sub>2</sub> and CO photoreduction in our laboratory, both completed. In these experiments, the Ti centers are utilized as chromophores and excited redox sites. Direct evidence for the precise nature of these active sites by XAFS combined with in-situ infrared monitoring of the photochemistry has furnished the first insight into the primary reaction steps of carbon oxide reduction in these nanoporous reactors.<sup>1,2</sup>

We have accomplished hydrothermal synthesis of a microporous RuAlPO<sub>4</sub> material. The importance of such a material lies in the known role of Ru in CO<sub>2</sub> chemistry. Preliminary characterization by powder X-ray diffraction, scanning electron microscopy, and UV-visible spectroscopy indicates a sieve with predominant AFI structure and reversibly reducible Ru sites. L-edge measurements in the in the 2800-3000 eV range revealed two sharp absorptions whose separation as function of oxidative/reductive treatment will allow us to assign the oxidation states of the Ru in the material.

## REFERENCES

1. N. Ulagappan and H. Frei, "Mechanism of CO<sub>2</sub> photoreduction in TS-1 molecular sieve," J. Phys. Chem., submitted.
2. Y.H. Yeom and H. Frei, "Photoreaction of CO with CH<sub>3</sub>OH in microporous Ti silicalite," J. Phys. Chem., submitted.

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